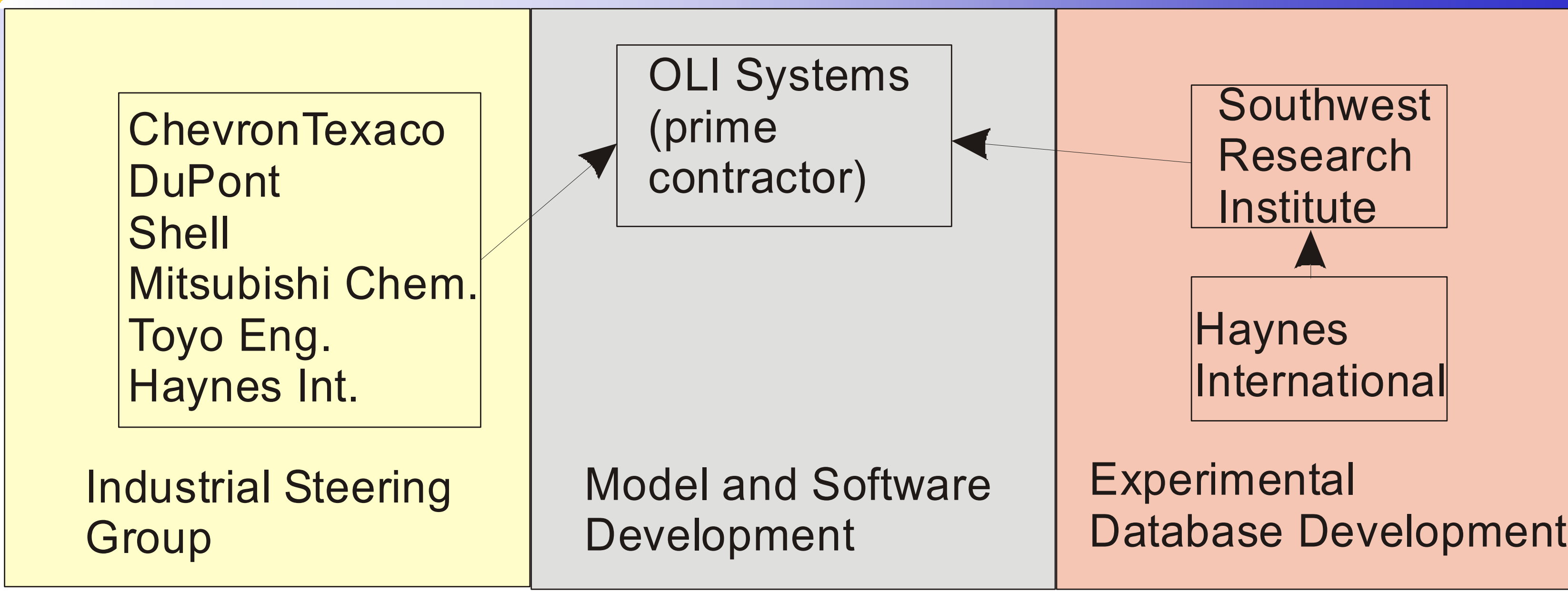
Prediction of Corrosion of Advanced Materials and Fabricated Components

OLI systems, Inc.

Project Team



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Prediction of Corrosion of Advanced Materials and Fabricated Components

Summary

- **Goal:** Develop software tool for predicting localized corrosion of process equipment including fabricated components as well as base alloys
- **Challenge:** There is no generally accepted basis for judging the corrosion performance of materials in process environments without performing specific tests. Recently developed prediction methods need to be parameterized for complex environments and extended to fabricated materials.
- **Benefits:** Allow process designers and operators to evaluate materials under realistic conditions of fabrication and chemical environments, identify process changes, inhibition strategies; energy savings of 8.8e13 Btu/year
- **FY05 activities:** Development of microchemistry database and electrochemical parameter database, parameterization of models, relating electrochemical parameters to alloy composition

- Participants:
  - OLI Systems Inc.
  - Southwest Research Institute
  - Haynes International
  - ChevronTexaco
  - DuPont
  - Shell
  - Mitsubishi Chemical
  - Toyo Engineering

Barrier, Pathway and Metrics

Barriers

- Lack of tools to evaluate performance of metals prior to placing them in service

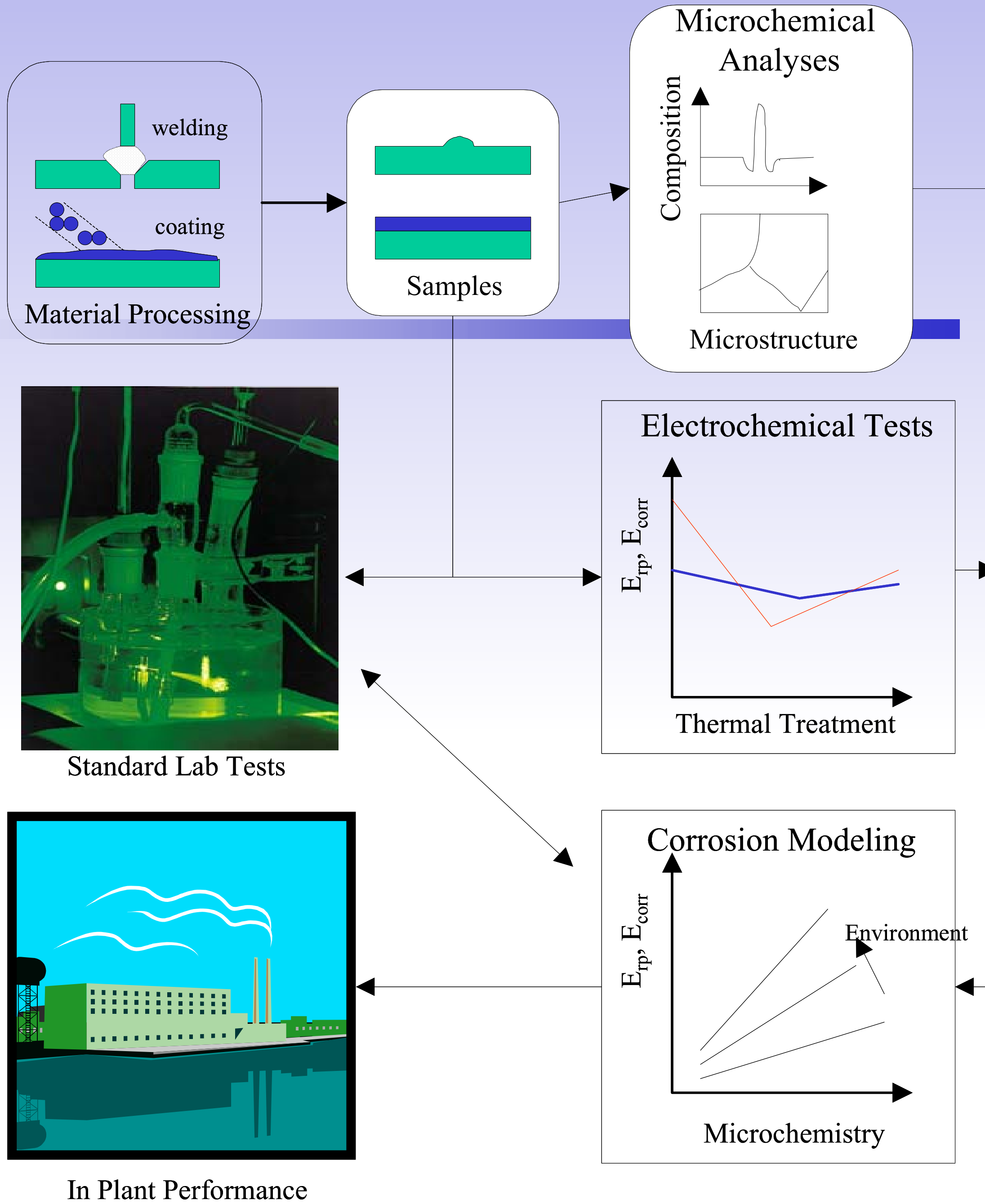
Pathways:

- Correlate local composition of alloys with parameters that govern localized corrosion (corrosion and repassivation potentials)
- Correlate localized corrosion parameters with solution chemistry
- Develop a model for predicting remaining life based on short-term data
- Encapsulate the model in software – a virtual testing laboratory

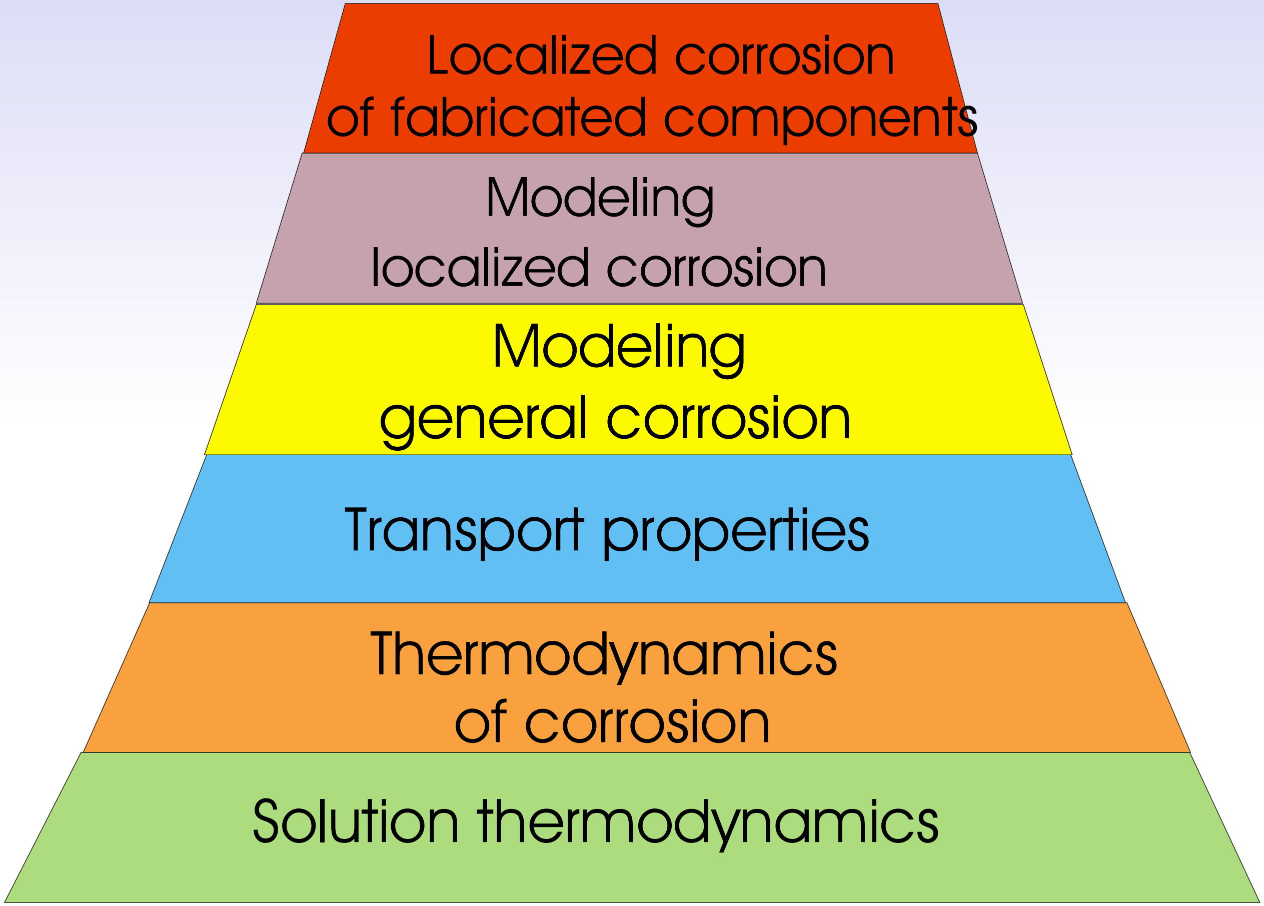
Metrics:

- Validate the accuracy of prediction of corrosion and repassivation potentials as functions of environment
- Verify the agreement of the model with standard tests for base alloys and fabricated materials
- Verifying the validity of methods for predicting remaining life

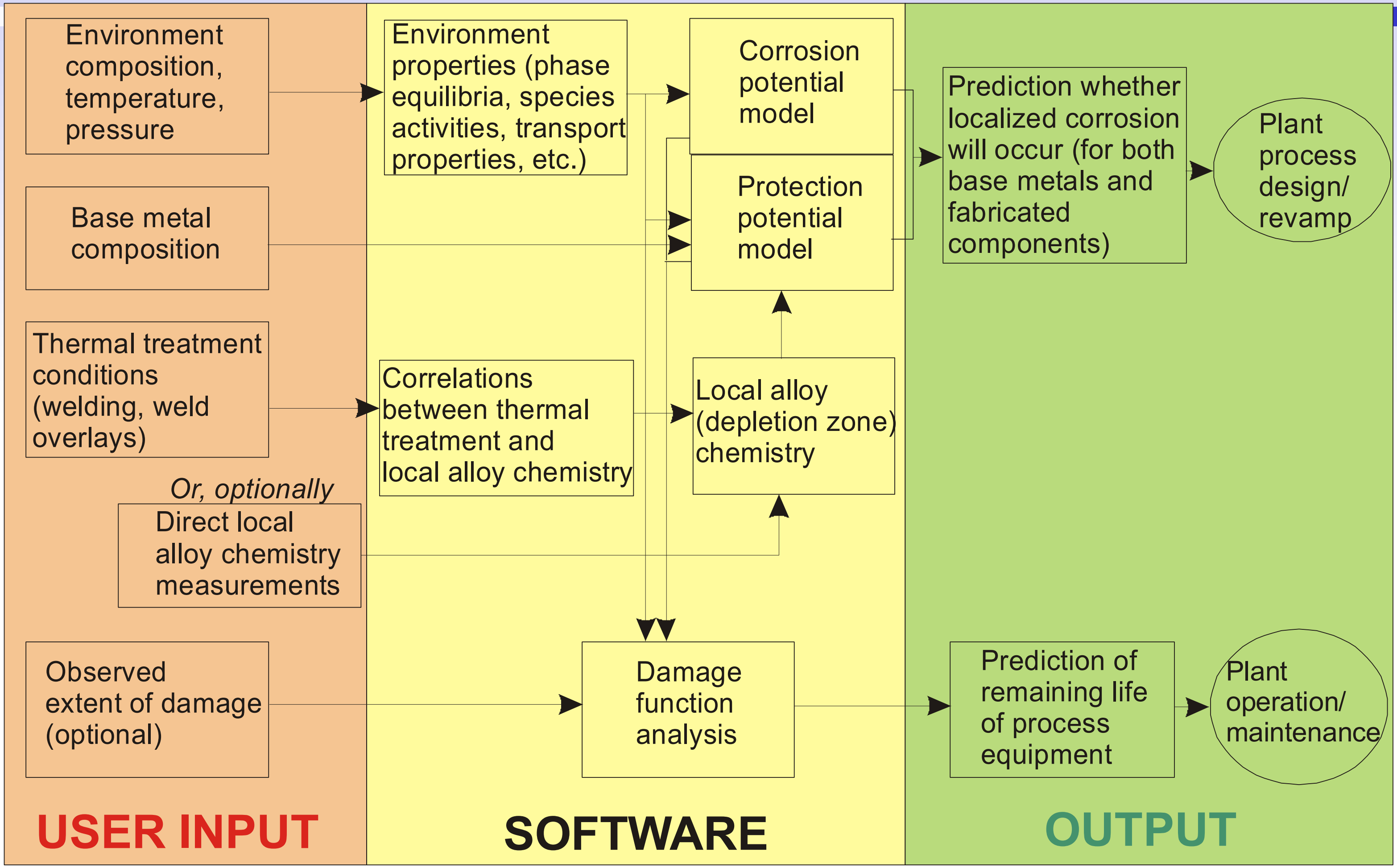
Schematic view of the approach



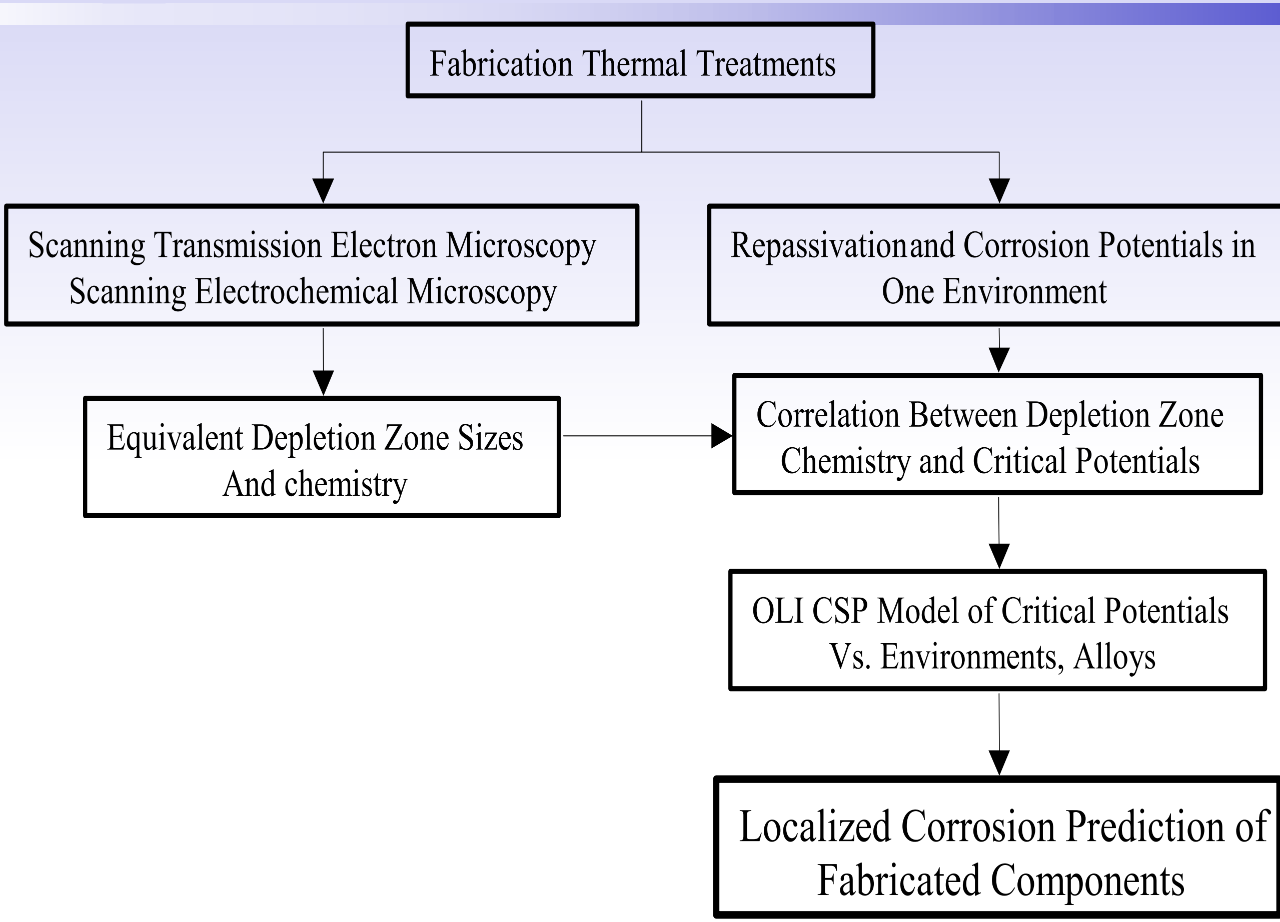
Structure of models for simulating aqueous corrosion



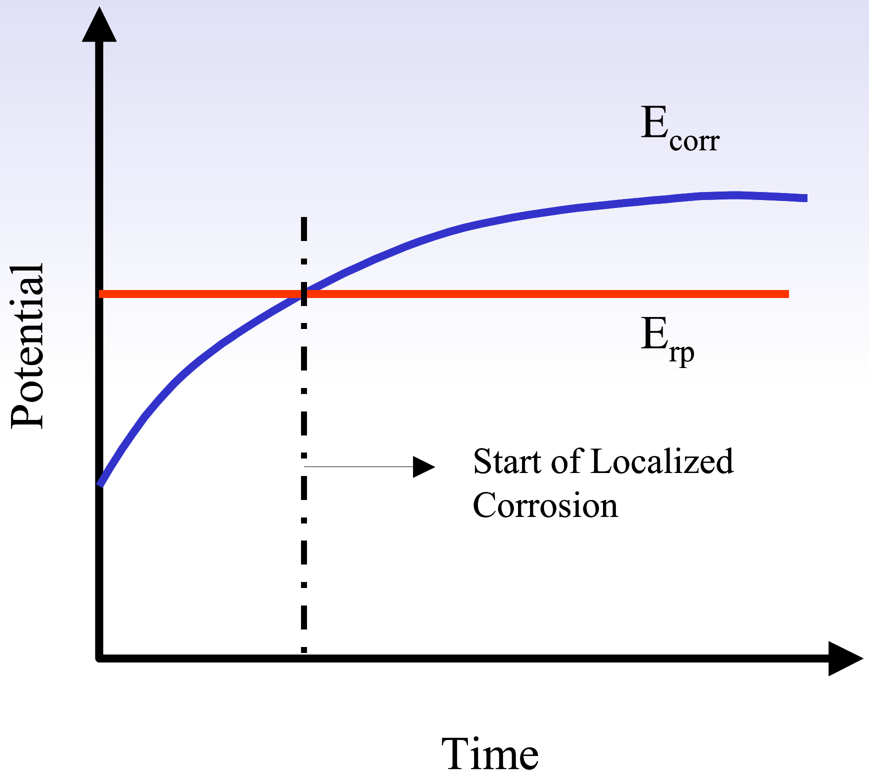
Vision of localized corrosion software after three years



Overall Technical Approach

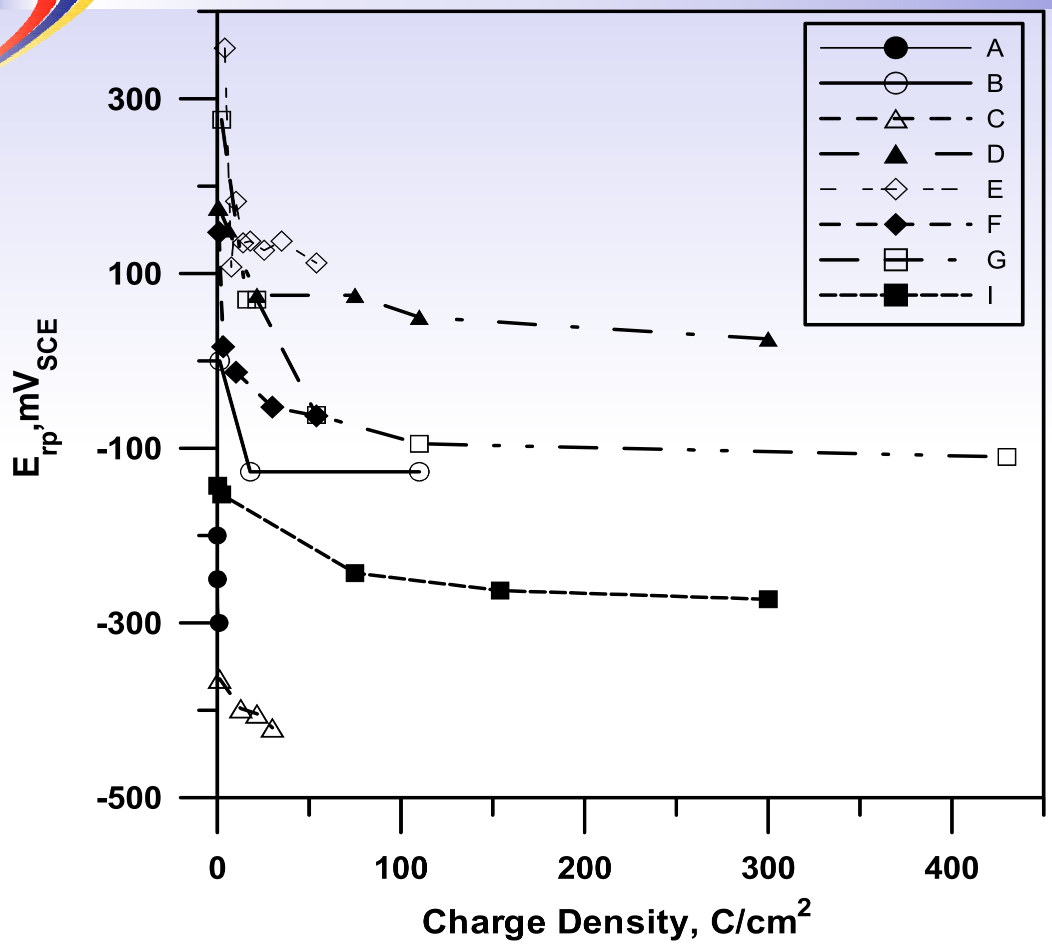


Localized Corrosion: Overall Predictive Approach



- Localized corrosion occurs when the corrosion potential exceeds a critical potential
- Repassivation potential is used as a critical potential
- Approach: Develop models for predicting the repassivation potential and corrosion potential as functions of solution chemistry and temperature

Validity of the repassivation potential for predicting the occurrence of localized corrosion



- The repassivation potential attains a lower-bound value as the pit or crevice depth increases
- It provides a conservative threshold parameter

Experimental Program

- Repassivation potential measurements

Alloy	Condition	Tests
Phase I		
316L	Base	Inhibitors (OH^-, SO_4^{2-}, MoO_4^{2-}, NO_2^-, VO_3^{2-})
	Heat Treatment to Simulate Weldments	E_{rp}
	Weldment	E_{rp}
2205	Base	Inhibitors (OH^-, SO_4^{2-}, MoO_4^{2-}, NO_2^-, VO_3^{2-}), E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}
	Weldment	E_{rp}
Alloy 600	Base	Inhibitors (OH^-, SO_4^{2-}, MoO_4^{2-}, NO_2^-, VO_3^{2-})
	Heat Treatment to Simulate Weldments	E_{rp}
Alloy 690	Base	Inhibitors (OH^-, SO_4^{2-}, MoO_4^{2-}, NO_2^-, VO_3^{2-})
C-276	Base	Inhibitors (OH^-, SO_4^{2-}, MoO_4^{2-}, NO_2^-, VO_3^{2-})
	Heat Treatment to Simulate Weldments	E_{rp}
	Weldment	E_{rp}
	Casting	E_{rp}
254SMO	Base	Inhibitors (OH^-, SO_4^{2-}, MoO_4^{2-}, NO_2^-, VO_3^{2-})
Monel	Base	E_{rp}
CuNi 70-30	Base	E_{rp}
Phase II		
G-35	Base	E_{rp}
	Weldment	E_{rp}
Monel	Weldment	E_{rp}
CuNi 70-30	Weldment	E_{rp}
CuNi 90-10	Base	E_{rp}
	Weldment	E_{rp}
Zr 702	Base	E_{rp}
	Weldment	E_{rp}
Experimental #1	Base	E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}
Experimental #2	Base	E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}
Experimental #3	Base	E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}
Phase III		
Ti-Grade 2	Base	E_{rp}
	Weldment	E_{rp}
Ti-Grade 26/28	Base	E_{rp}
	Weldment	E_{rp}
Al 7075	Base	E_{rp}
	Weldment	E_{rp}
Carbon Steel Overlay	Base	E_{rp}
	Weldment	E_{rp}
Experimental #4	Base	E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}
Experimental #5	Base	E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}
Experimental #6	Base	E_{rp}
	Heat Treatment to Simulate Weldments	E_{rp}

Experimental Program

- Corrosion potential measurements

Alloy	Type of sample	Corrosion potential measurement
	Phase I	
316L	Weld	Oxygen, ferric effects
C-276	Base metal, weld	ferric effect
Monel	Base metal	Oxygen effect as a function of pH
	Phase II	
G-35	Base metal, weld	Ferric effect
CuNi 70-30	Base metal	Oxygen effect as a function of pH
2205 Duplex SS	Base metal, weld	Oxygen, ferric effects
Zr 702	Base metal	Oxygen effect as a function of pH
CuNi 90-10	Base metal	Oxygen effect as a function of pH
	Phase III	
Al 7075/2024	Base metal	Oxygen effect
Ti-Grade 2, 26/28	Base metal	Oxygen effect as a function of pH
Carbon steel	Base metal, overlay	Ferric effect

Experimental Program

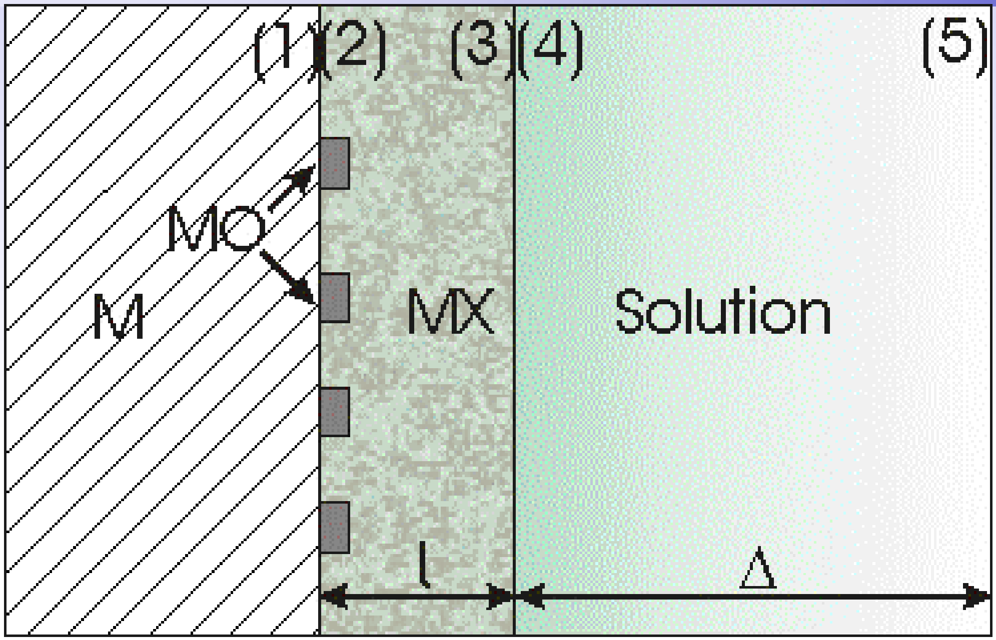
- Long-term measurements

Alloy	Type of Sample	Experiment
2205 duplex SS	Base metal crevice	Constant potentials above and below repassivation potential
Al 7075/2024	Base metal crevice	Constant potentials above and below repassivation potential
Zr-702	Base metal	Constant potentials above and below repassivation potential

- Tests for measuring damage growth and distribution

Alloy	Type of sample	Environment	Experiment
316L	Base metal	Three levels of Cl concentration and three levels of potential will be selected (chloride and potential will be selected to obtain a meaningful distribution of pits)	Maximum pit depth distribution and number of pits per unit area
2205 duplex SS	Base metal, weld		
C-276	Base metal, weld		

Predicting the repassivation potential: Physical background of the model



Potential drop across the interface:

$$E = \Delta\Phi_{M/MX}(1,2) + \Delta\Phi_{\mathrm{MX}}(2,3) + \Delta\Phi_{MX/S}(3,4) + \Delta\Phi_{S}(4,5)$$

Fundamentals of the E_{rp} model

- The expressions can be solved in the limit E -> E_{rp}

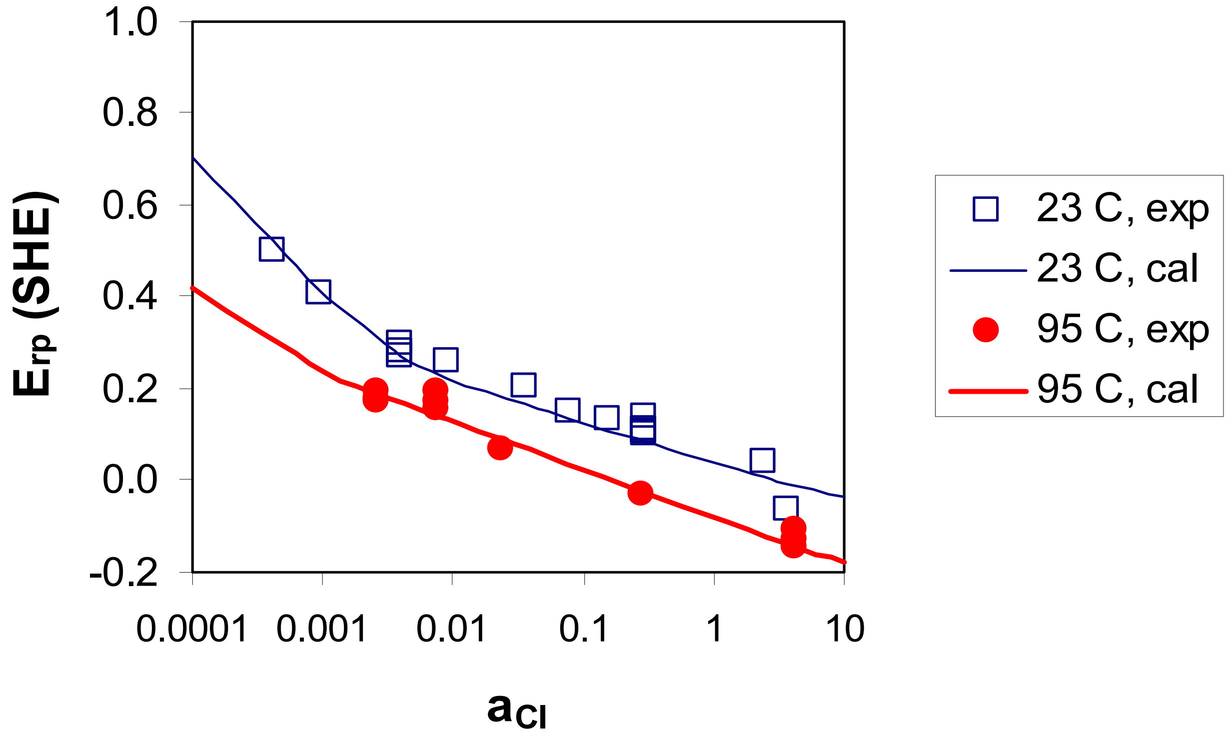
$$1+\sum_j\left[\left(\frac{i_{rp}}{i_p}-1\right)\frac{l_j''}{i_{rp}}\right]\theta_j^{n_j}\exp\left(\frac{\xi_j F E_{rp}}{RT}\right)=\sum_i\frac{k_i''}{i_{rp}}\theta_i^{n_i}\exp\left(\frac{\alpha_i F E_{rp}}{RT}\right)$$

Contributions of water and inhibiting species, which participate in oxide formation in the repassivation process

Contributions of aggressive species, which form complexes with metal species

Application of the model:

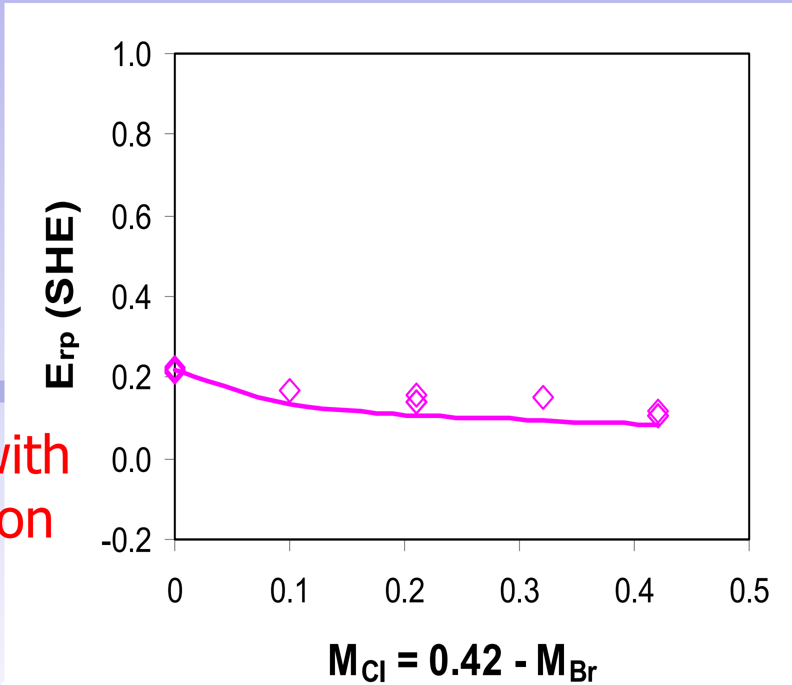
E_{rp} for 316L in Cl solutions



- Two slopes are reproduced by the model
- They result from the competition between the dissolution of metal-halide complexes and the formation of oxide

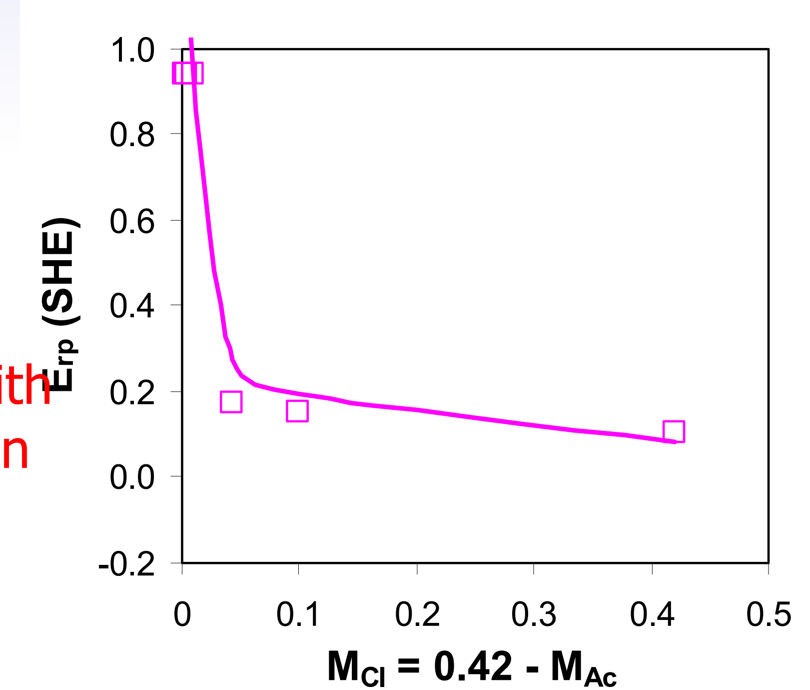
Modeling the repassivation potential:
Effects of Cl^-, Br^- and Ac^- ions for 316L SS

Cl^- + Br^- solution with a total concentration of 0.42 M

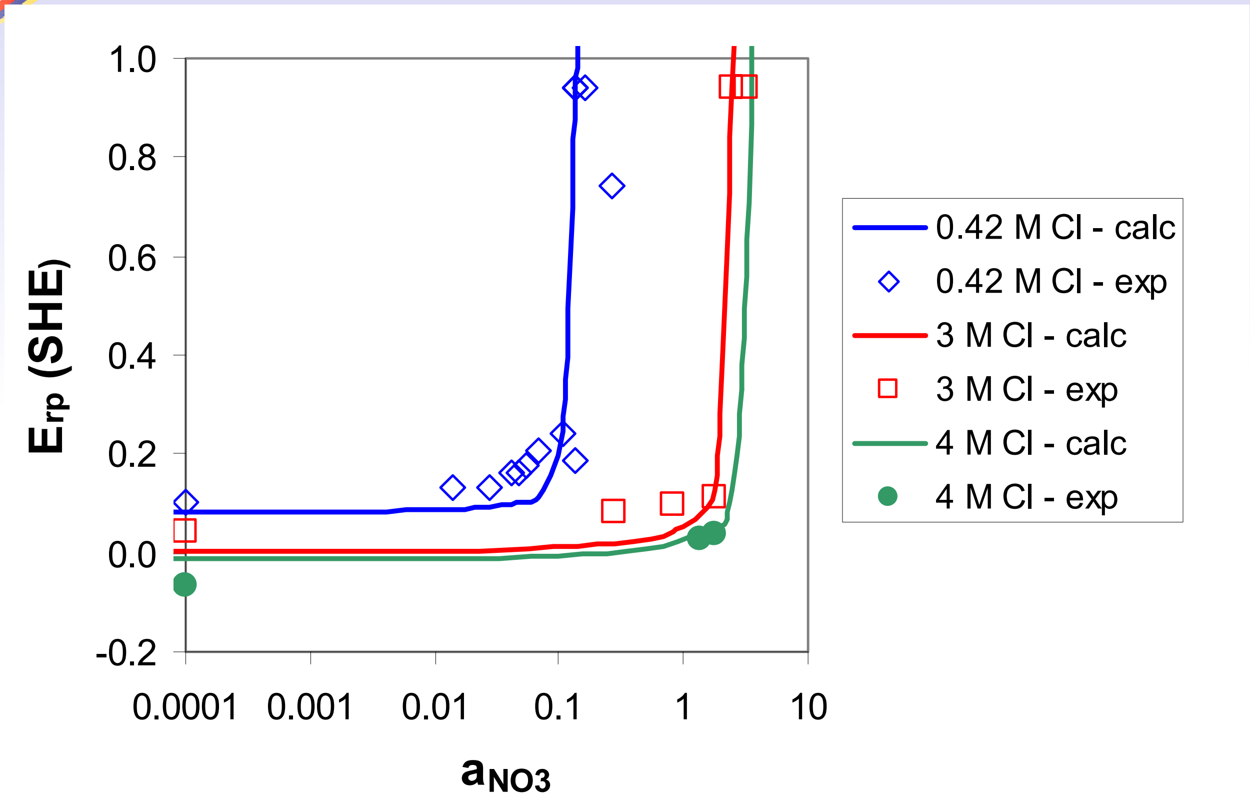


Mixing chlorides with other aggressive ions or nonaggressive ions

Cl^- + Ac^- solution with a total concentration of 0.42 M

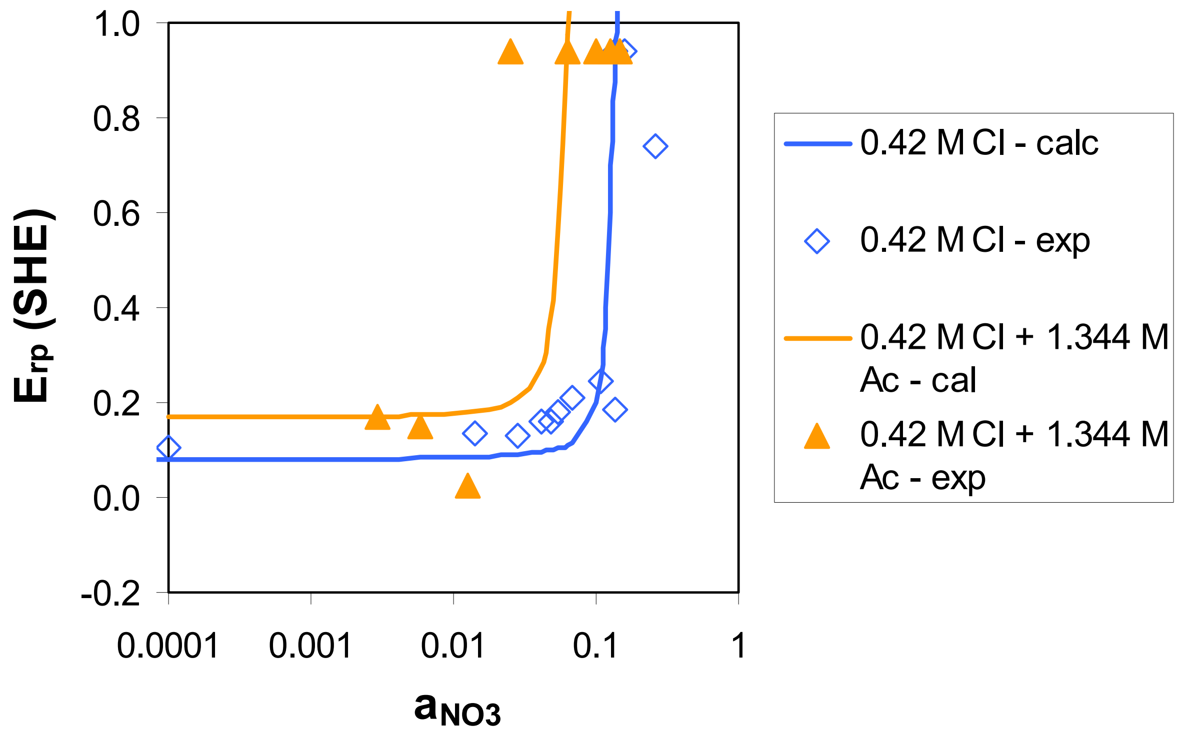


Modeling the repassivation potential:
Effect of strongly inhibitive ions



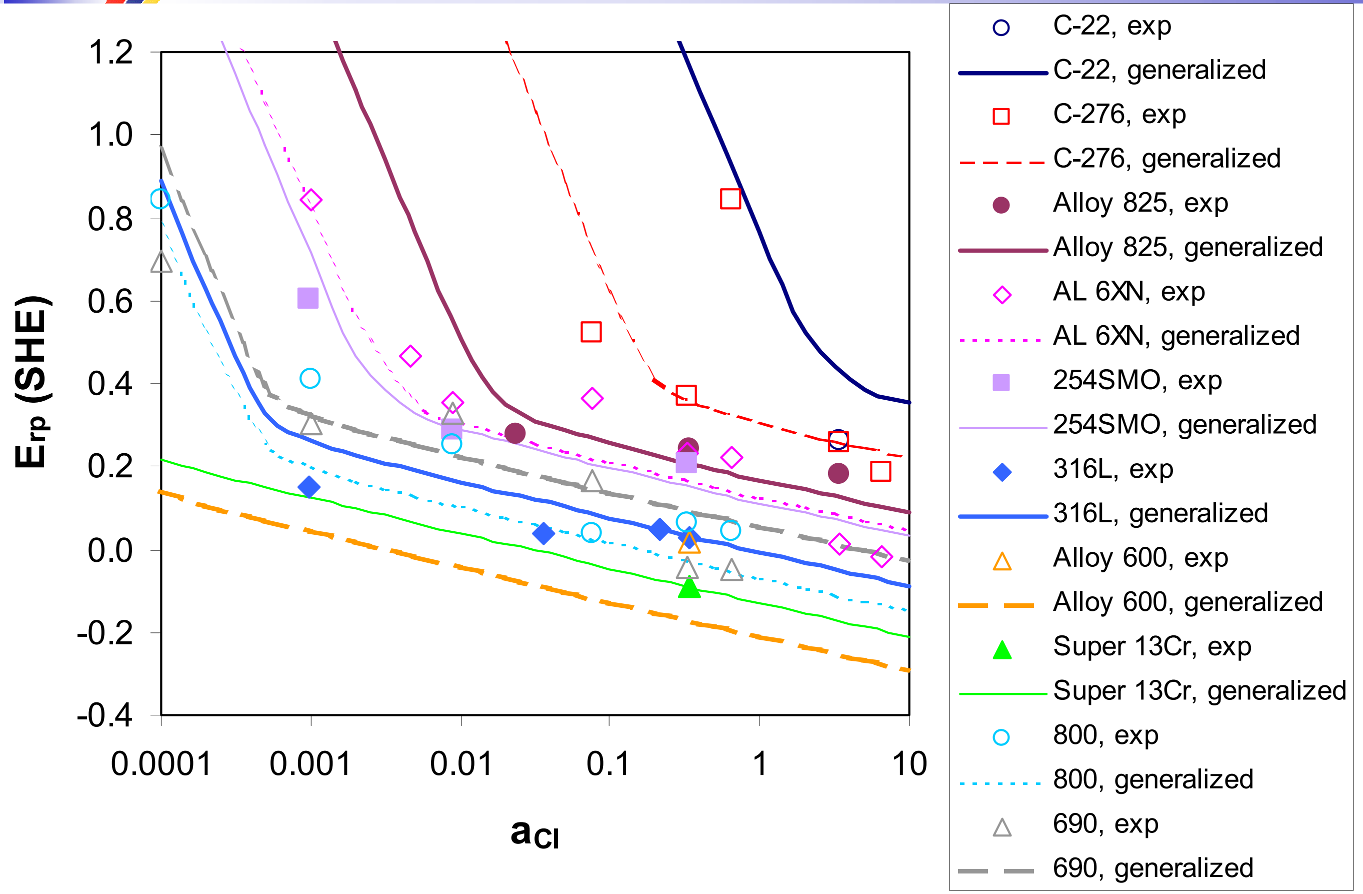
- E_{rp} of type 316L SS as a function of nitrate activity for selected chloride concentrations

Modeling the repassivation potential: *Prediction for multicomponent systems*



- E_{rp} in a mixed Cl^- + NO_3^- with or without 1.344 M CH_3COO^-

Generalized correlation for the repassivation potential of Fe-Ni-Cr-Mo-W alloys

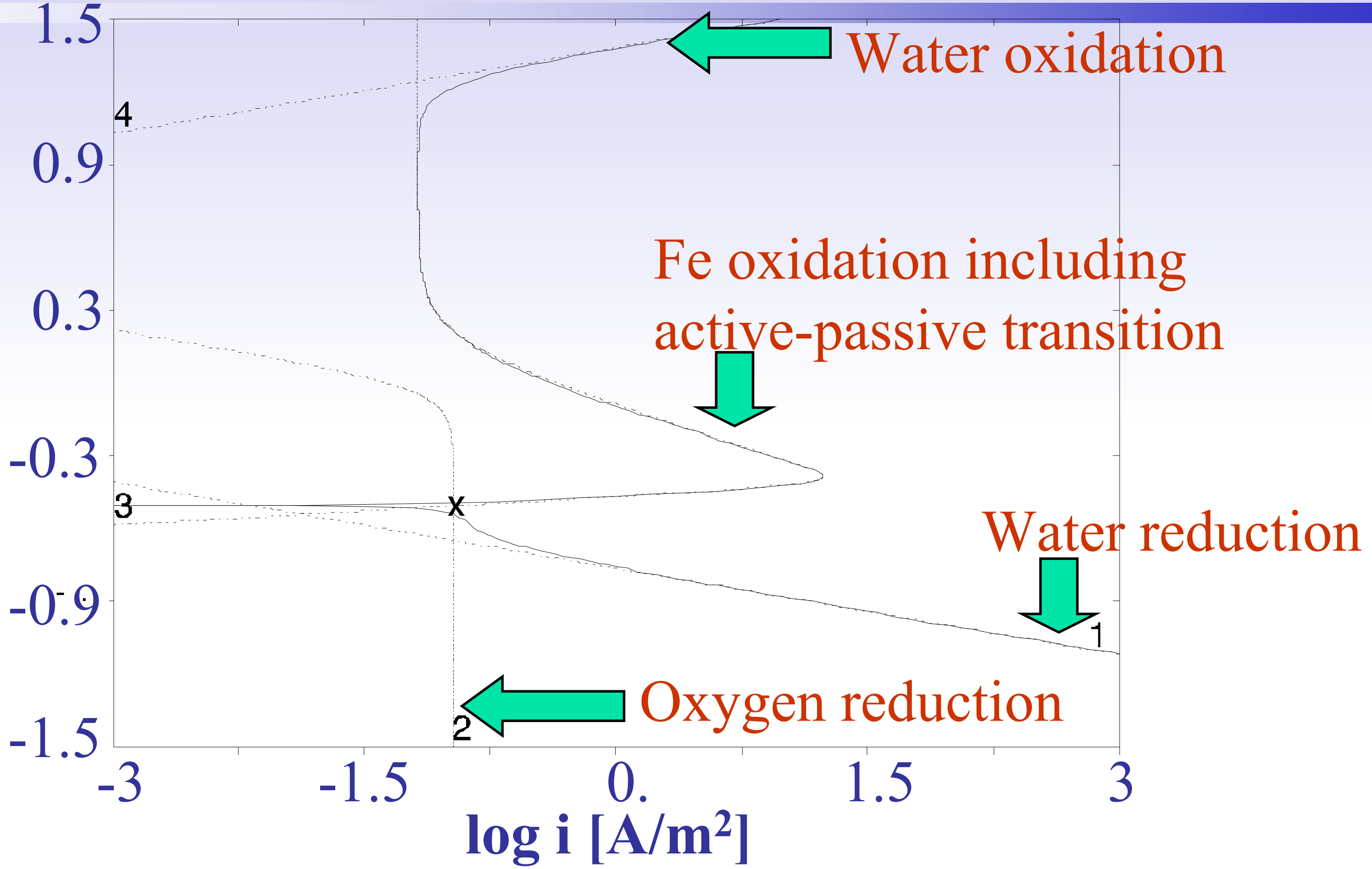


- Results for 333 K
- Alloys 690 and 800 were not included in the database for establishing the parameters; they provide a test of the correlation

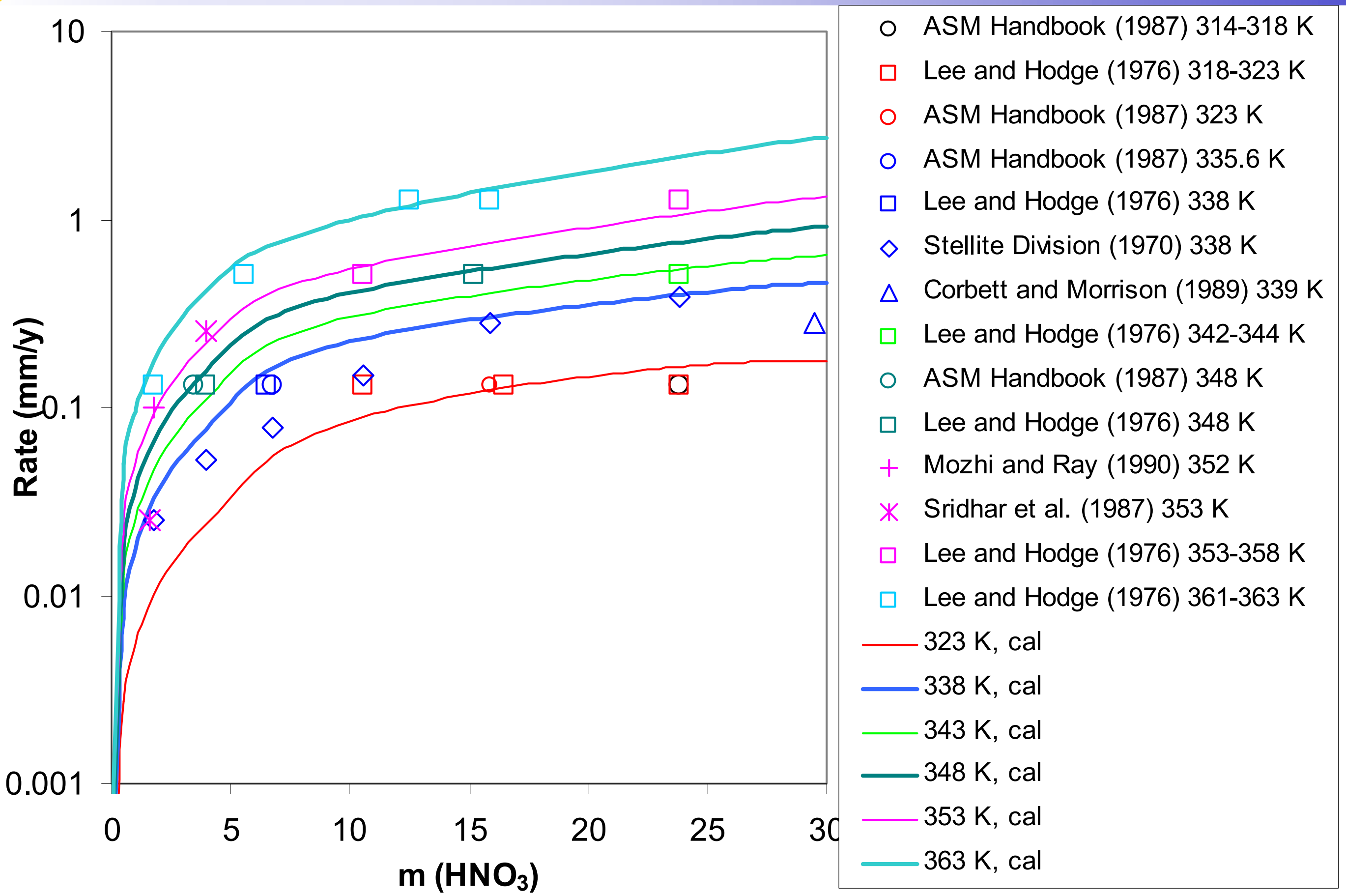
Predicting the corrosion potential
Electrochemical model for general corrosion

- Partial electrochemical processes in the active state:
  - Cathodic reactions (e.g., reduction of protons, water molecules, oxygen, etc.)
  - Anodic reactions (e.g., oxidation of metals)
- Active-passive transition influenced by
  - Acid/base properties of passive oxide films
  - Temperature
  - Additional species that influence the dissolution kinetics of oxide layers
- Synthesis of the partial processes according to the mixed potential theory

How does the model work? Predicted current density - potential relationship for carbon steel in aerated H_2O

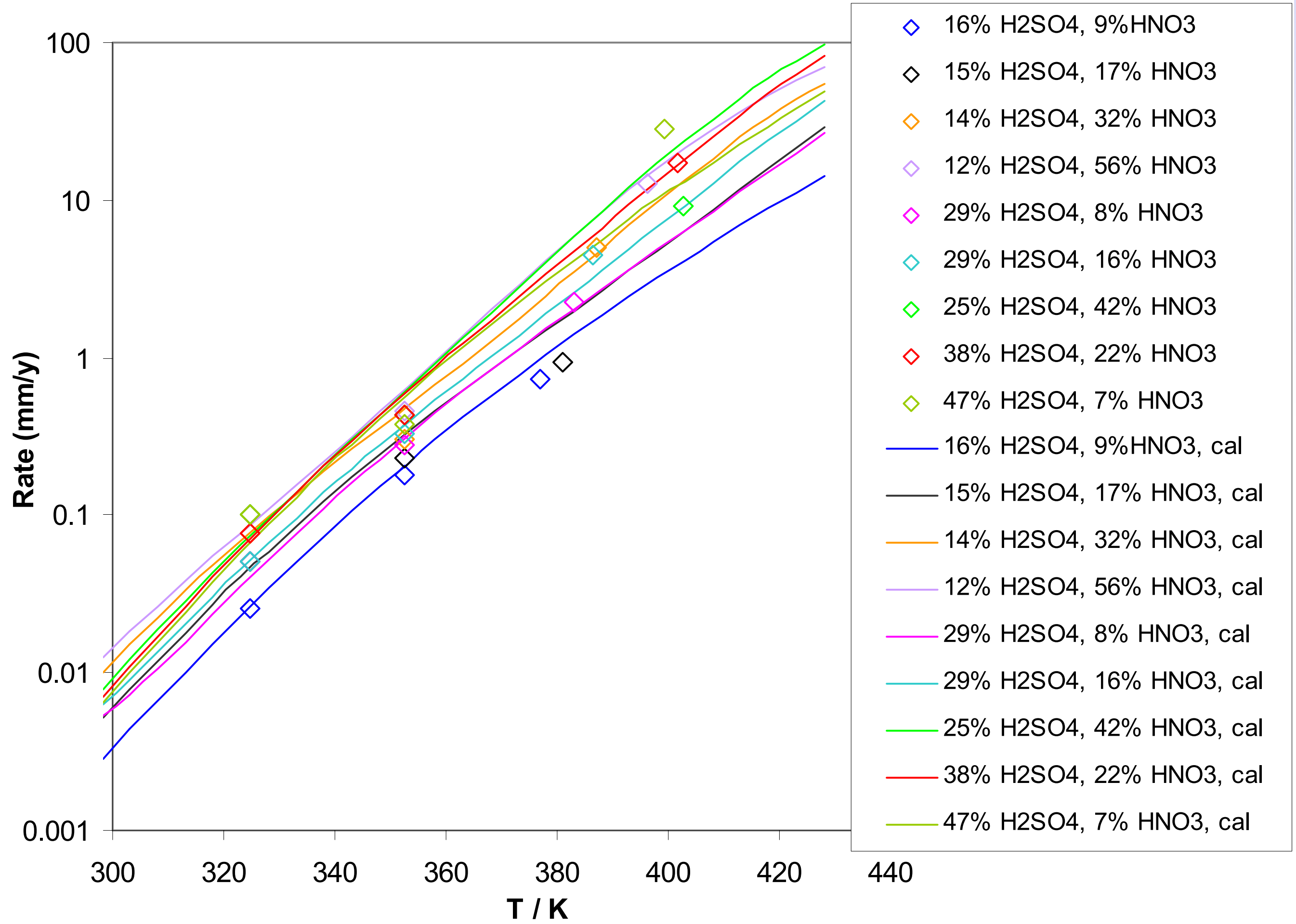


Applications of the general corrosion model: Alloy C-276 in HNO_3

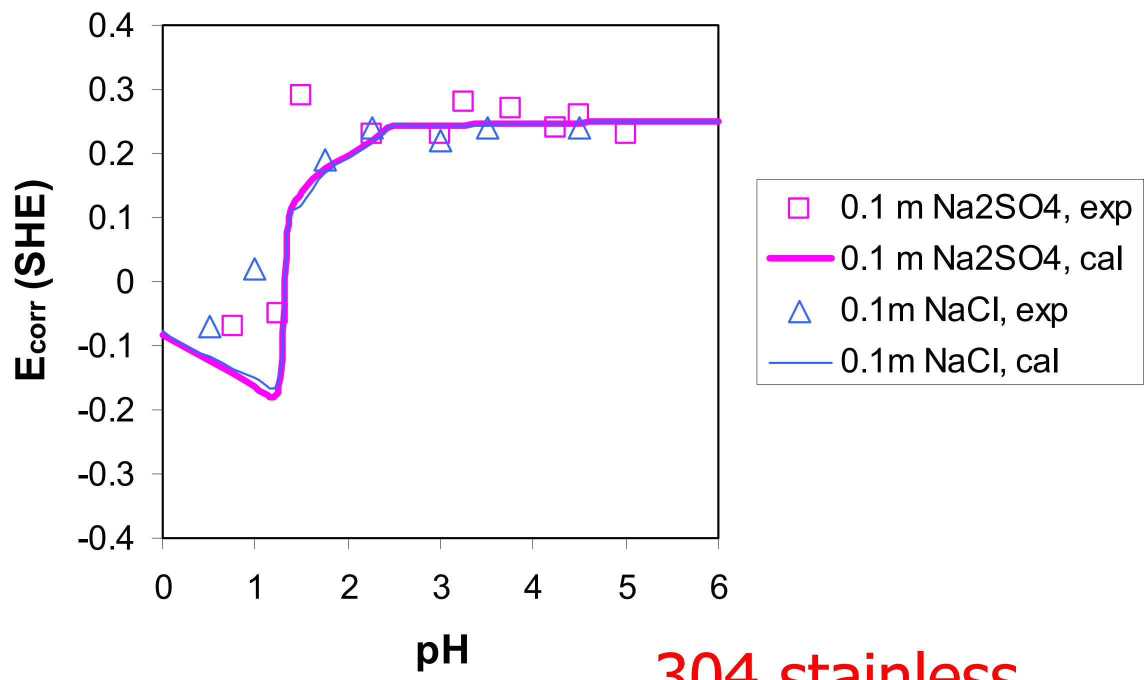


General corrosion in mixed acids:

Alloy C-276 in H_2SO_4 + HNO_3



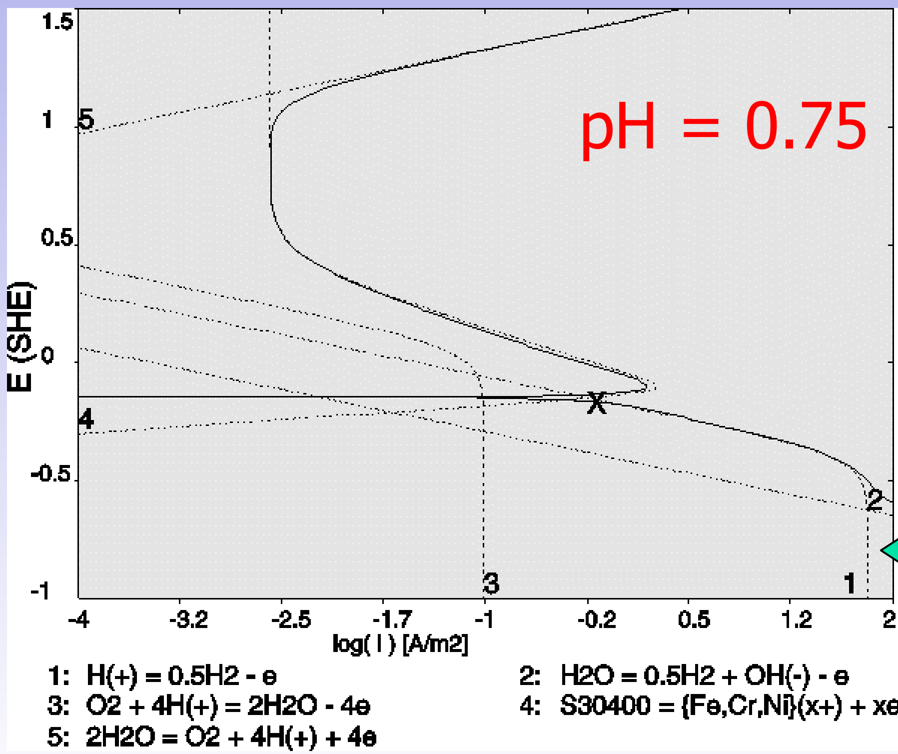
Effect of pH on the corrosion potential in aerated solutions



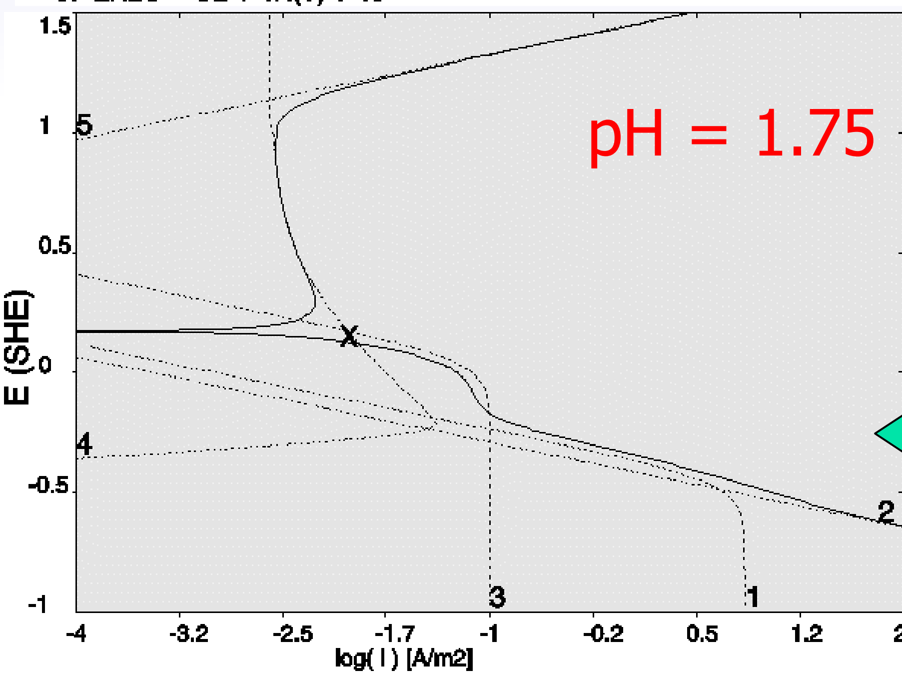
304 stainless steel

- Depassivation pH is characteristic for stainless steels and Ni alloys; it strongly depends on alloy composition
- E_{corr} on passive surfaces is similar for Fe-Ni-Cr-Mo alloys because of the presence of similar Cr oxides

How is this behavior modeled?

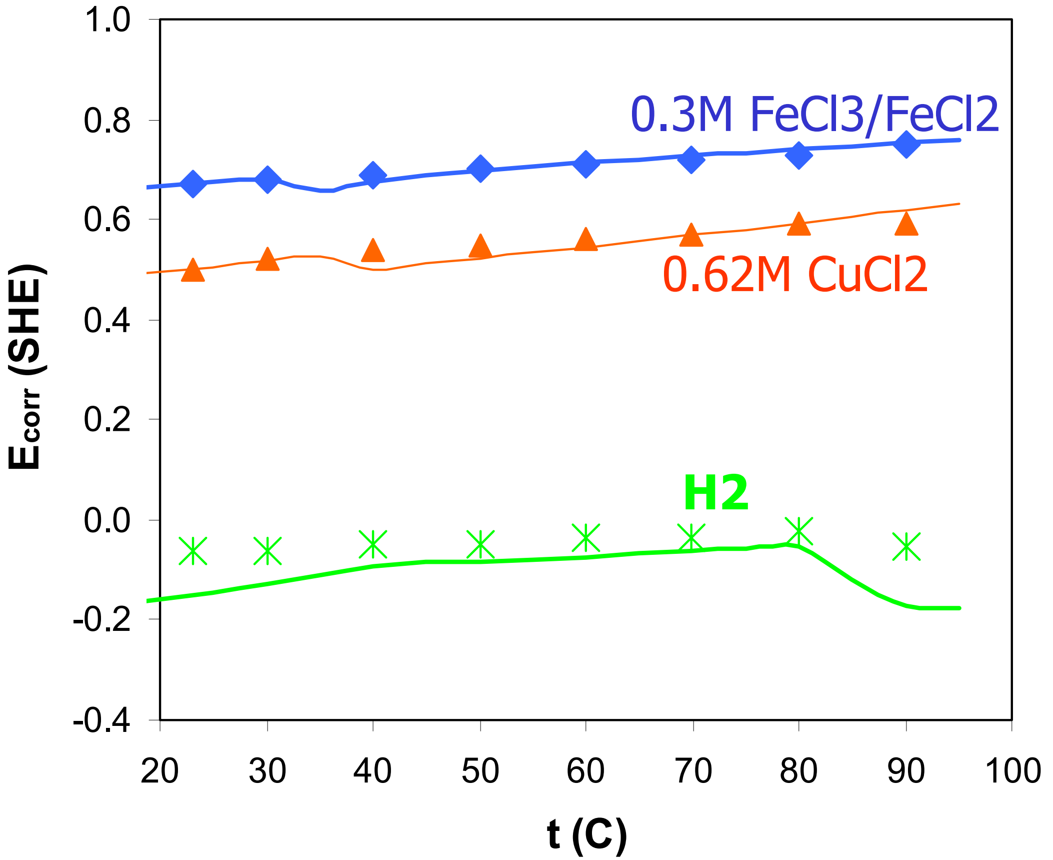


SS 304 corrodes in the active state



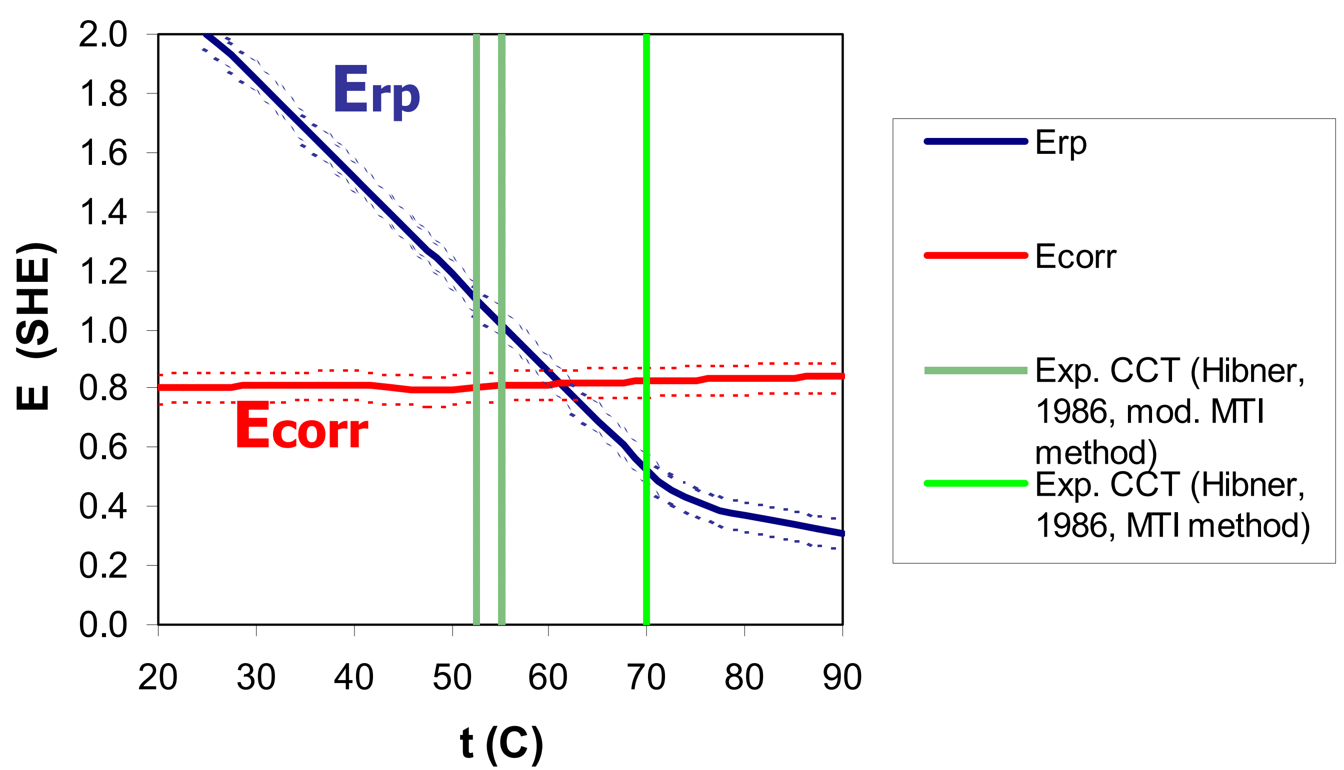
The mixed potential shifts to the passive state

Prediction of the corrosion potential for alloy C-22



- The general corrosion model reproduces the effect of redox species on the corrosion potential

Predicting critical crevice temperature for alloy C-22 in 6% $FeCl_3$ solutions



- Intersection of E_{corr} and E_{rp} corresponds to the critical crevice temperature
- Predicted CCT is in good agreement with experimental data

Prediction of Corrosion Damage: Probabilistic Approach

$$EVD = 1 - P_f = \exp\{-SF(x,t)\}$$

Extreme Value Distribution function (EVD): the probability that the depth of the deepest pit will be $\leq x$

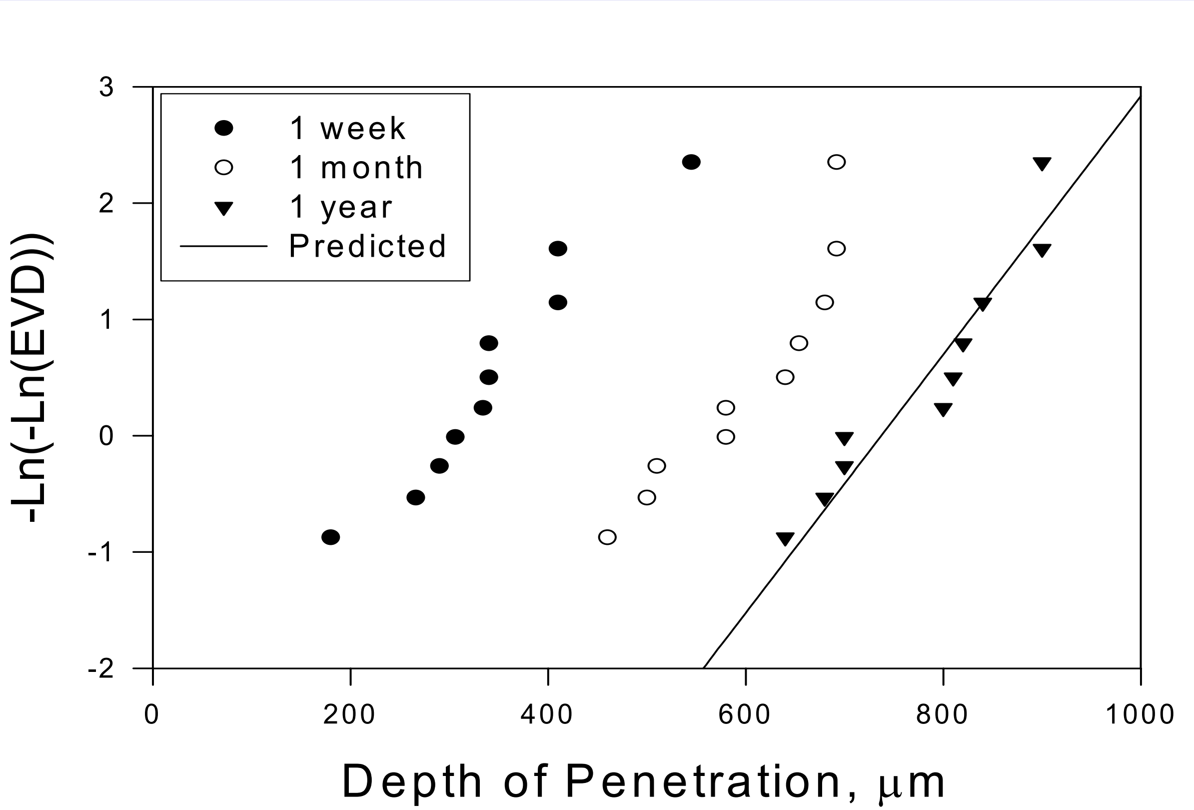
- P_f - probability of failure
- F is the integral damage function (per cm^2)
- **S** is the total area of the system.

OLI's Approach:

- Parameters that determine the damage function are calculated from EVD values obtained from short-term experiments using small samples
- Then, the probability of failure after a long period of time is predicted

Prediction of long-term corrosion damage
Corrosion of aluminum in tap water

Extreme value distribution



Only data for t = 1 week and t = 1 month are used for fitting.

Experimental data from P. M. Aziz., *Corrosion*, **12**, 495 (1956).